

N-coordinated single cobalt atoms catalyst triggering concerted radical-nonradical process in catalytic ozonation for efficient water decontamination



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ABSTRACT

Heterogeneous catalytic ozonation (HCO) has been developed as a promising technology for wastewater treatment, while traditional radical-based HCO process still suffers from insufficient mineralization of organic pollutants. Herein, we constructed a N-coordinated single cobalt atoms catalyst (CoSAC-N-C) triggering concerted radical-nonradical process in catalytic ozonation for efficient decontamination of pollutants. Experiments and theoretical calculations proved that mediate O in O_3 obtained electrons from electron-rich N sites for hydroxyl radical ($\cdot\text{OH}$) production, and the terminal O in O_3 was attracted on electron-deficient Co sites for nonradical $^*\text{O}$ generation by O-O cleavage. The synergistic oxidation of $\cdot\text{OH}$ and $^*\text{O}$ enabled excellent pollutants mineralization, surpassing most of conventional HCO catalysts. CoSAC-N-C exhibited excellent treatment performance for the coking wastewater in a continuous-flow reactor with COD reducing from 86 mg/L to less than 50 mg/L. This work provided a viable strategy of developing dual-site HCO catalysts to promote concerted radical-nonradical oxidations for wastewater treatment.

1. Introduction

With ever-growing demand for clean water and safe ecological environment, the development of highly efficient and environmentally friendly wastewater treatment technologies is urgently needed [1–3]. Heterogeneous catalytic ozonation (HCO) has been recognized as one of promising wastewater treatment technologies due to its high efficiency in mineralizing organic pollutants, catalyst recyclability and few reagent residue [4,5]. In a typical HCO process, ozone molecules are decomposed on active sites to generate reactive species for contaminants removal. The HCO process can be assigned to radical and nonradical oxidation pathways, according to the types of reactive species [6,7].

In radical-based HCO process, the strongly oxidative hydroxyl radical ($\cdot\text{OH}$, $E^0=1.9\text{--}2.7\text{ V}_{\text{SHE}}$) can be generally generated on catalysts via decomposition of ozone, which is highly efficient to degrade most of organic pollutants in water [8,9]. However, the radical-based HCO process suffered the disadvantage of insufficient mineralization for real wastewater treatments, which results from sluggish elimination of

small-molecule carboxylate intermediates as well as the competitive consumption of $\cdot\text{OH}$ by background ions [9]. The limited decontamination of $\cdot\text{OH}$ -dependent oxidation process can be improved by coupling with nonradical active species [10–12]. For example, Guo et al. indicated that the synergistic oxidation of radicals and nonradicals were superior to single active species for effective degradation of organic pollutants in complex actual wastewater, in which strongly oxidative radical $\cdot\text{OH}$ deconstruct pollutants without selectivity and mild oxidative nonradical $^1\text{O}_2$ can selectively degrade sulfamethoxazole in the presence of background interference [11]. Among the nonradical-based HCO processes ($^*\text{O}$, $^*\text{O}_2$ and $^1\text{O}_2$), the surface atomic oxygen $^*\text{O}$ with high oxidation potential ($E^0=2.43\text{ V}_{\text{SHE}}$) was reported to show resistance to coexisting ions as well as selective degradation towards small-molecule carboxylates, such as oxalic acid commonly produced as main degradation byproducts [10,13]. In light of the unique advantages of radical $\cdot\text{OH}$ and nonradical $^*\text{O}$ species, we speculated that rapid pollutants removal and enhanced mineralization performance could be achieved by coupling radical and nonradical degradation pathways in HCO

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process. During the synergistic radical-nonradical oxidations, the organic pollutants could be first degraded into small organic acid by $\cdot\text{OH}$ and then further mineralized to CO_2 and H_2O by $^*\text{O}$. Therefore, it is vital to design the catalysts with dual-active sites to drive the concerted radical-nonradical oxidation pathway for improving the mineralization performance of organic wastewaters. Currently, most researches focused on the exploration of individual radical or nonradical species production, while the design of HCO catalysts for simultaneously inducing radical-nonradical oxidation pathways remains to be challenging due to the insufficient understanding on structure-activity relationships in catalytic ozonation.

Single atom catalysts (SACs) are emerging as a promising catalyst owing to their well-defined catalytic sites, unique atomic structure and electronic property, which show high selectivity and efficiency in catalysis [14–16]. In SACs, atomically dispersed metal (M) can be anchored on carbon by coordinating with N dopants, forming M-N₄ configuration. The strong electronegativity of N atoms in M-N₄ coordination can tune the electron density of metal atoms, forming dual centers of electron-rich N sites and electron-deficient metal sites [12, 17–19]. As reported, the decomposition process of ozone molecules for reactive species generation depended on the different charge distributions of active sites [5, 17, 20]. Therefore, it is reasonable to believe that preparing single atom catalyst possessing dual reaction sites with different charge distribution can regulate reactive species production and provides a great possibility to steer concerted radical-nonradical oxidation reactions.

In this work, we designed a catalyst of single Co atoms coordinated with N in carbon support (Co_{SAC}-N-C) with dual reaction sites driving concerted radical-nonradical oxidation pathway for efficient organic pollutants mineralization. Based on experimental and theoretical results, we found that the electron-rich N sites tended to bond with mediate O in O_3 molecule and provided electron to O_3 for radical $\cdot\text{OH}$ generation, while electron-deficient Co sites attracted terminal O of O_3 for nonradical $^*\text{O}$ generation by O-O cleavage. Benefited from the synergistic oxidation of $\cdot\text{OH}$ and $^*\text{O}$, Co_{SAC}-N-C exhibited superior mineralization performance to conventional HCO catalysts. The experimental results showed that the organic pollutants can be firstly destructed by $\cdot\text{OH}$ into small organic acids and then were further mineralized by $^*\text{O}$. Moreover, Co_{SAC}-N-C exhibited excellent treatment performance for the coking secondary effluent in a continuous-flow reactor with COD reducing from 86 mg/L to less than 50 mg/L. Our findings provided a promising strategy for developing efficient HCO catalysts with synergistic radical-nonradical oxidations in wastewater treatment.

2. Materials and methods

2.1. Chemical and reagents

Dopamine hydrochloride (DA, 99%), Cobalt acetylacetone (Co(acac)₂, 99%), 2,2,6,6-tetramethylpiperidine (TEMP, 99%), benzoic acid (BA, 99%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 99%), 4-nitrophenol (4-NP, 99%), levofloxacin (LVFX, 99%), carbamazepine (CBZ, 99%), acetaminophen (APAP, 99%) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Methanol (HPLC grade) and acetonitrile (HPLC grade) were purchased from Merck. Spherule γ -Al₂O₃ particles in 2–3 mm diameter were provided by Shanghai Macklin Biochemical Co., Ltd. Salicylic acid was obtained from Sigma-Aldrich. Other chemicals and reagents were provided by Damao chemical Co., Ltd. All chemical reagents were used without further treatment. Ultrapure water with a resistivity of 18 M Ω ·cm was used throughout the experiments.

2.2. Synthesis of catalysts

Typically, 2 mL ammonia aqueous solution was added in the mixture of 36 mL ethanol and 94 mL ultrapure water under stirring for 10 min,

which is denoted as solution I. Then, 500 mg DA and 5.7 mg Co(acac)₂ were dissolved in the mixed solution with 6 mL ethanol and 4 mL ultrapure water, which is denoted as solution II. Solution II was slowly injected into solution I under stirring for 48 h at room temperature. The resultant precipitates were collected by centrifugation at 8000 rpm and washed with water and ethanol for five times, followed by drying at 60 °C for 6 h in an oven. Thereafter, the precursors were transferred into a tube furnace and carbonized at 750 °C (or the desired temperatures) under flowing argon gas for 2 h with the heating rate of 2 °C min⁻¹. Finally, the catalyst was obtained after washing with 2 M HCl for 12 h at 80 °C. For comparison, we also prepared the metal-free N-doped carbon (N-C) and cobalt nanoparticle supported on N-doped carbon (Co_{NP}-N-C). The details of preparation information were shown in Text S1.

2.3. Characterization of catalysts

Morphology of the catalysts was observed on scanning electron microscope (SEM, NOVA NanoSEM, Thermo Fisher, USA) and transmission electron microscopes (TEM, TF30, Thermo Fisher, USA) with an energy dispersive spectrometer (EDS). The atomic-scale images of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of catalysts were obtained by using STEM (JEM-ARM200F) with a spherical aberration corrector. The X-ray diffraction patterns (XRD) were detected with SmartLab with Cu K α radiation. The X-ray absorption spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the sample at Co-edge was conducted in fluorescence mode on beamline 12-BM in the Advanced Photon Source at Argonne National Laboratory. The surface elemental composition and chemical states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, k-Alpha+, Thermo Fisher, USA). Raman spectroscopy (Thermo Fisher, USA) were conducted by DXR Microscope ($\lambda_{\text{exc}}=532$ nm). The Brunauer-Emmett-Teller (BET) specific surface area and pore-size distribution of catalysts were measured by a sorption analyzer Autosorb-IQ-C (Quantachrome, USA) at 77 K. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 2000 DV, PerkinElmer, USA) is employed to determine the metal contents of catalysts or metal leaching in reaction solutions. The signals of generated reactive oxidative species were detected by electron paramagnetic resonance spectrometer (EPR, A200-9.5/12, Bruker, Germany). The zeta potentials were recorded with a zeta potential analyzer (ZS90, Malvern, UK). The linear sweep voltammetry (LSV) measurements were carried out in a convention three-electrode cell system with a CHI 700E electrochemical workstation (Chenhua Instrument, Shanghai, China).

2.4. Catalytic ozonation experiments

All semi-batch experiments were conducted in a 500 mL column reactor (effective volume is 250 mL) at 25±0.2 °C with a magnetic stirring speed of 500 rpm. Ozone was generated by an ozone generator (COM-AD-01, Anshan Anseros Environmental Protection Co., Ltd, Anshan, China). Typically, a certain mass of catalyst was dispersed in a 250 mL solution containing 20 mg/L oxalic acid (OA). Ozone (gas concentration 20 mg/L) was then bubbled into the reactor at a flowrate of 0.2 L min⁻¹. The O_3 in off-gas was adsorbed by 5 wt% KI solution. At predetermined time intervals, the samples were taken and quenched by 0.1 M Na₂S₂O₃, then filtered through 0.22- μm polytetrafluoroethylene membrane for analysis.

The treatment of actual wastewater from secondary effluent of coking plant (Guangxi, China) was conducted in a continuous-flow reactor. Briefly, the reactor was filled with 200 g catalyst of Co_{SAC}-N-C-loaded alumina pellets (Co_{SAC}-N-C@Al₂O₃, detailed preparation information was shown in Text S1) with net volume of ~500 mL. The system reached adsorption-desorption equilibrium after continuous flowing for 2 h. Then, ozone (gas concentration 10 mg/L) was bubbled into the reactor at a flowrate of 1.0 L min⁻¹ to trigger the degradation

reaction. The hydraulic retention time (HRT) was 40 min.

The analytical methods are shown in the Text S2 and Table S1.

3. Results and discussion

3.1. Catalyst characterizations

As schematically illustrated in Fig. 1a, the catalyst was prepared by polymerization-pyrolysis strategy. Briefly, cobalt salt was added in dopamine solution, which polymerized in alkaline solution to form Co (acac)₂@polydopamine (Co-PDA) [21]. Afterwards, the as-prepared Co-PDA was subjected to inert annealing and acid leaching to obtain the catalyst. The SEM and TEM images (Fig. 1b-d) showed that the catalyst displayed a nanosphere with uniform diameters of 400 nm, and no obvious nanoparticles or clusters were observed on the surface of catalysts. The corresponding EDS mapping (Fig. 1e) showed the homogeneous distribution of Co, N and C elements. Furthermore, HAADF-STEM was employed to investigate Co dispersion at the atomic level. The monodispersed bright spots corresponding to isolated Co atoms were observed over the N-doped carbon matrix in Fig. 1f, confirming the atomic dispersion of Co species in Co_{SAC}-N-C. The Co content in Co_{SAC}-N-C was measured to be 0.45 wt% by ICP-OES. The XRD

pattern of Co_{SAC}-N-C resembled with that of N-C exhibiting two characteristic peaks at 25° and 44°, which referred to graphite carbon plane (Fig. 1g). No characteristic peaks of metal-containing species were observed on Co_{SAC}-N-C, excluding the existence of crystalline Co species [22]. Moreover, the Raman spectrum (Figure S1a) of Co_{SAC}-N-C and N-C exhibited D and G bands at 1341 and 1586 cm⁻¹, respectively, verifying the formation of graphitized carbon [23,24]. The N₂ adsorption-desorption isotherms of Co_{SAC}-N-C showed the feature of microporous structure with the average pore size of around 2 nm (Figure S1b-c). The catalyst of Co_{SAC}-N-C had a higher specific surface area and pore volume (511.35 m²/g 0.189 cm³/g) compared to NC (Table S2), which was favorable to exposing active sites for O₃ decomposition.

The chemical states of catalysts were investigated by XPS analysis. The XPS survey spectrum indicated the coexistence of C, N and Co in Co_{SAC}-N-C (Figure S2a). The high-resolution Co 2p showed weak spectral signals due to the low metal loading in catalyst (Figure S2b). The N 1s of Co_{SAC}-N-C showed a slight down-shift (0.24 eV) of pyridinic N peak compared with N-C (Figure S2c), which was attributed to the strong coordination between Co atoms and pyridinic N [25,26]. To further explore the coordination information of Co sites of Co_{SAC}-N-C, XANES and EXAFS of the Co K-edge were examined. Here, we took

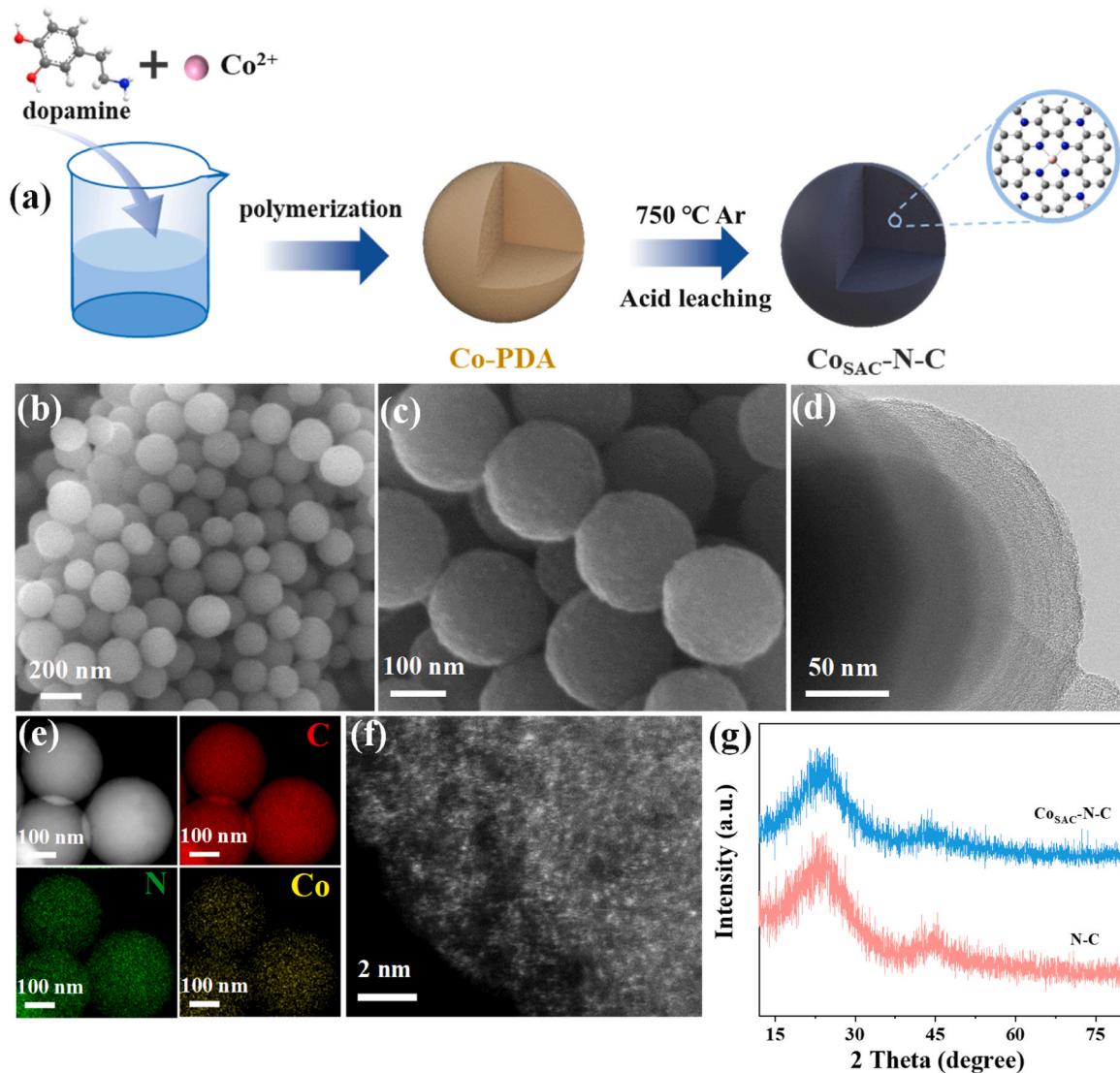


Fig. 1. (a) Schematic illustration of the synthesis procedure of Co_{SAC}-N-C. (b-c) SEM images, (d) TEM image, (e) EDS mapping of C, N and Co. (f) HAADF-STEM image of Co_{SAC}-N-C. (g) XRD patterns of N-C and Co_{SAC}-N-C.

$\text{Co}_{\text{SAC}}\text{-N-C}$ for example and several standard Co species (e.g., Co foil, CoO , Co_3O_4 and CoPc) as references. In the Co K-edge spectra (Fig. 2a), the absorption threshold position of $\text{Co}_{\text{SAC}}\text{-N-C}$ was higher than that of Co foil, suggesting single Co atoms carried positive charges. According to the first-derivative XANES curves of $\text{Co}_{\text{SAC}}\text{-N-C}$ and references in Figure S3, the average oxidation state of Co atoms was approximately +2.1 [27,28]. The FT-EXAFS curves for $\text{Co}_{\text{SAC}}\text{-N-C}$ only showed a prominent peak at 1.4 Å corresponding to Co-N bond (Fig. 2b), no Co-Co (2.49 Å) and Co-O (1.91 Å) peak was detected, indicating the absence of metallic crystalline Co species [29]. Furthermore, compared with references of Co foil, Co_3O_4 and CoPc , the WT-EXAFS of Co atom in $\text{Co}_{\text{SAC}}\text{-N-C}$ presented only one maximum value at (1.65 Å, 4.85 Å⁻¹), which originated from Co-N coordination (Fig. 2c). It confirmed atomically dispersed Co in $\text{Co}_{\text{SAC}}\text{-N-C}$, consistent with the HAADF-STEM and XRD results. The detailed coordination configuration of Co species was further investigated by quantitative least-squares EXAFS curve-fitting. The fitting results of EXAFS of the $\text{Co}_{\text{SAC}}\text{-N-C}$ revealed that Co atom was coordinated with four N in the first shell at average distances of 1.99 Å (Fig. 2d, Figure S4 and Table S3). Based on above analysis, it was concluded that Co species was atomically dispersed with the coordination structure of Co-N_4 in $\text{Co}_{\text{SAC}}\text{-N-C}$. In addition, the characterization of TEM, EDS and XPS for $\text{Co}_{\text{NP}}\text{-N-C}$ were shown in Figure S5. The Co 2p XPS deconvolution results of $\text{Co}_{\text{NP}}\text{-N-C}$, the characteristic peak at 782.45/798.5 eV, 780.75/796.8 eV and 779.15/795.85 eV were assigned to Co^{3+} , Co^{2+} and Co^0 , respectively. Besides, the TEM image of $\text{Co}_{\text{NP}}\text{-N-C}$ verified the existence of Co nanoparticle. The EDS results also indicated the agglomeration of Co on $\text{Co}_{\text{NP}}\text{-N-C}$.

3.2. Catalytic performance

The HCO activity of catalysts was first assessed with oxalic acid (OA) as the model pollutant, which was an ozone-recalcitrant organic contaminant ($k_{\text{OA}} < 0.04 \text{ M}^{-1} \text{ s}^{-1}$) [9]. As shown in Fig. 3a-d and Figure S6, the catalysts of $\text{Co}_{\text{SAC}}\text{-N-C}$ prepared at different temperatures exhibited higher performance for OA mineralization than metal-free catalyst (N-C) during HCO process, suggesting the important role of Co atoms for boosted O_3 catalytic activity. The degradation performance of $\text{Co}_{\text{SAC}}\text{-N-C}$ followed the consequence of 750 °C > 725 °C > 775 °C > 700 °C, of which the catalyst prepared at 750 °C with the highest catalytic activity was chosen for the following experiments. In control experiments, the sole ozonation showed only 14% TOC removal of OA within 60 min. Additionally, the $\text{Co}_{\text{SAC}}\text{-N-C}$ catalyst showed a limited contribution of adsorption to OA removal in the absence of ozone (Figure S7a). Impressively, OA was almost completely mineralized within 60 min in $\text{Co}_{\text{SAC}}\text{-N-C}$ HCO process with the kinetic rate constant of 0.0622 min⁻¹, even higher than homogeneous counterpart ($\text{Co}^{2+}/\text{O}_3$) (Fig. 3c-d). By contrast, less than 67% OA was mineralized within 60 min in $\text{Co}_{\text{NP}}\text{-N-C}/\text{O}_3$ system with lower kinetic constant (0.0128 min⁻¹) than $\text{Co}_{\text{SAC}}\text{-N-C}$, indicating the superior catalytic activity of single atom Co sites compared to Co nanoparticles in HCO process. For OA removal, the intrinsic specific activity of $\text{Co}_{\text{SAC}}\text{-N-C}$ based on turnover frequency (TOF, 0.0889 min⁻¹) (see Fig. 3e, Text S3 and Table S4 for more details) was higher than almost all of the state-of-the-art HCO catalysts reported so far, which demonstrated the admirable performance of $\text{Co}_{\text{SAC}}\text{-N-C}$ for pollutants removal in HCO process.

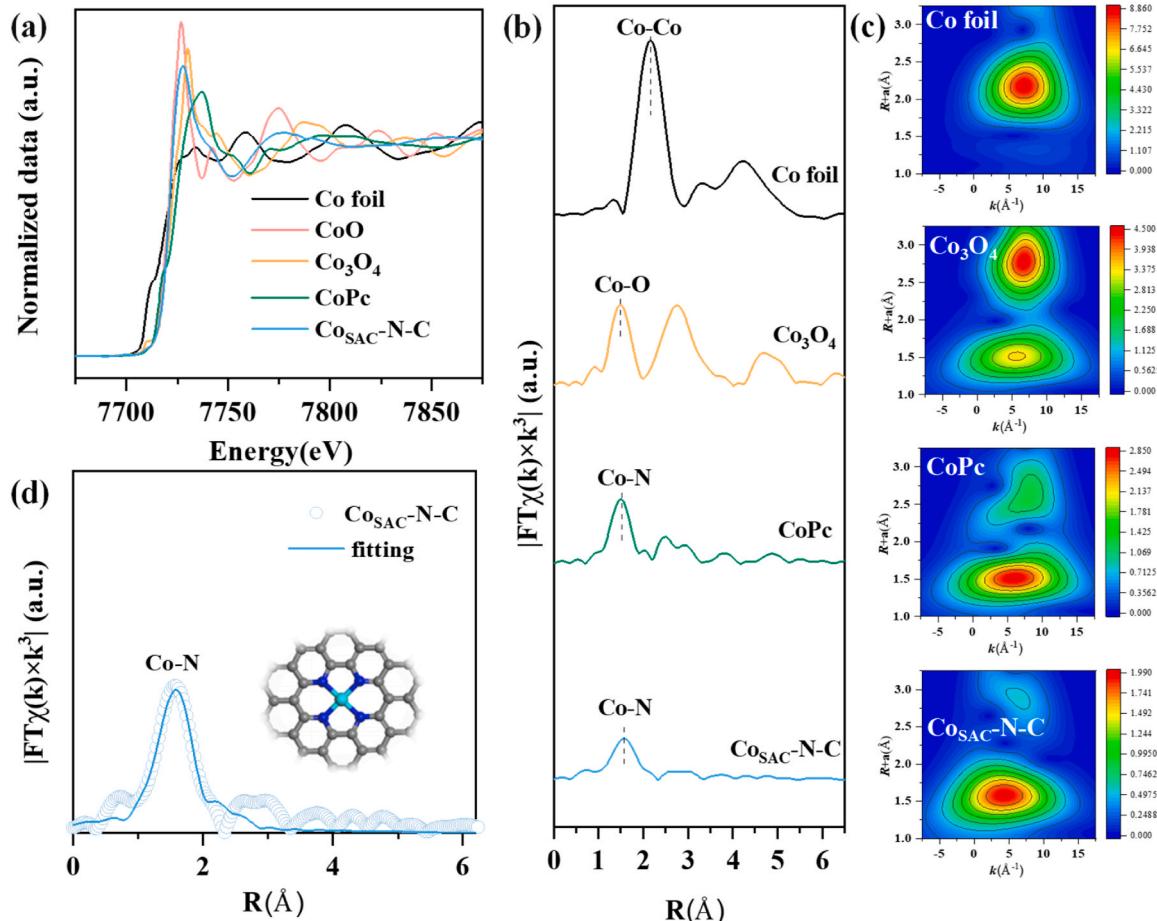


Fig. 2. (a) Normalized Co K-edge XANES spectra, (b) FT-EXAFS spectra and (c) WT-EXAFS of $\text{Co}_{\text{SAC}}\text{-N-C}$ and reference samples. (d) FT-EXAFS R-space fitting curve of $\text{Co}_{\text{SAC}}\text{-N-C}$ (inset: molecular model of the Co-N₄ site in $\text{Co}_{\text{SAC}}\text{-N-C}$ sample).

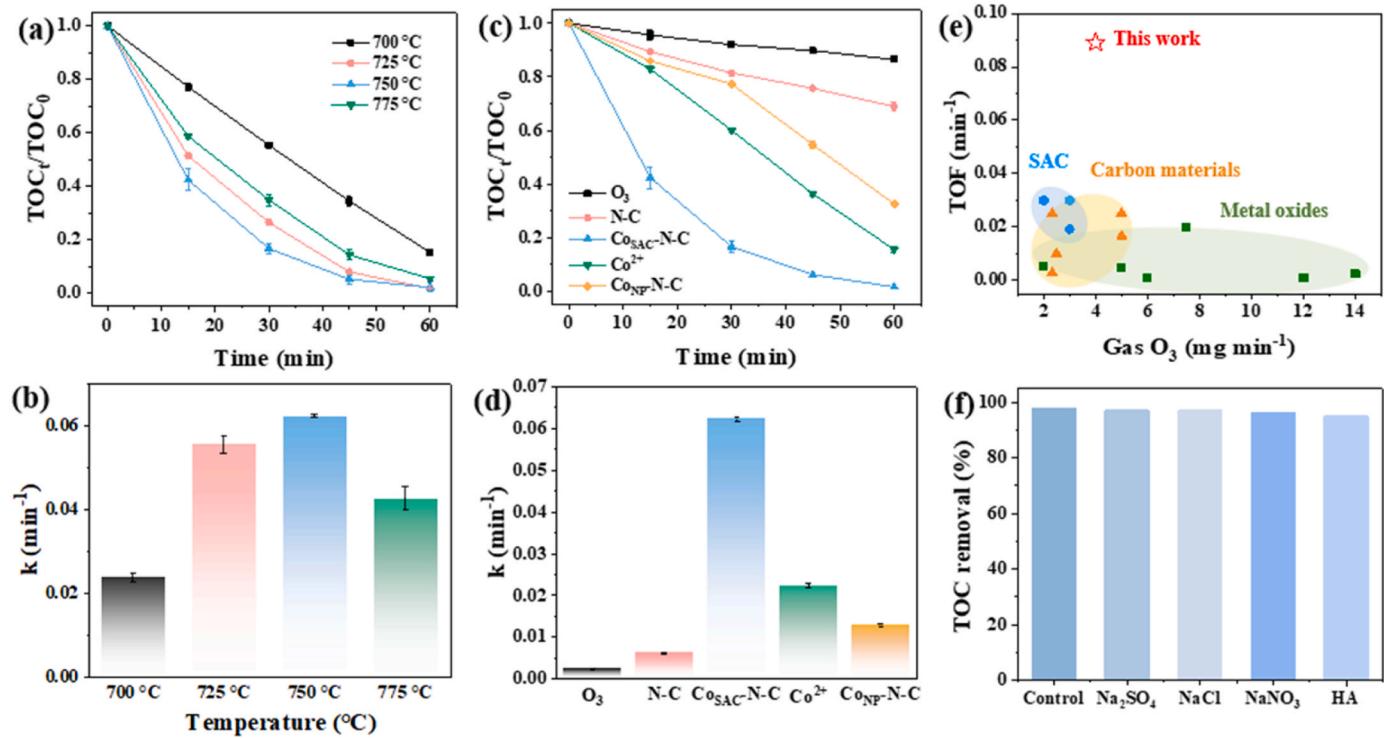


Fig. 3. (a) Mineralization of OA by Co_{SAC}-N-C with different pyrolysis temperatures, (b) their correspondent mineralization kinetic rate constants. (c) Mineralization of OA in different systems, (d) the correspondent mineralization kinetic rate constants. (e) Comparison of TOF for OA removal by state-of-the-art HCO catalysts. (f) Effects of anions and HA on TOC removal of OA. (Condition: [Co_{SAC}-N-C]=50 mg/L, [O₃]=20 mg/L, [OA]=200 mg/L, initial pH=2.9, [NaCl]=[Na₂SO₄]=[NaNO₃]=20 mM, [HA]=20 mg/L).

The impacts of catalysts dosage and O₃ concentration on OA abatement manifested the existence of optimum conditions, where the optimal dosage of the catalyst and O₃ were determined to be 50 mg/L and 20 mg/L (Figure S7c-d), respectively. The effect of initial pH on mineralization performance of Co_{SAC}-N-C was examined in Figure S8a-b. Under acidic conditions (pH=2.9–5.0), the kinetic rate constants of TOC removal decreased rapidly as pH rose. When pH increased to 7.0 and 8.9, the TOC removal was sluggish, while the rate constants changed slowly. The OA degradation mainly occurred on the catalyst surface. The electrostatic force between Co_{SAC}-N-C and OA would affect the TOC removal, which was depended on the point of zero charge (pH_{pzc}) of Co_{SAC}-N-C and the dissociation constant (pKa) of OA. The pH_{pzc} (pH at the point of zero charge) of ZFC-20% was around 5.3 (Figure S8c), suggesting the Co_{SAC}-N-C surface was negatively charged at pH of 7.0–8.9, higher than pH_{pzc}. The pKa value of OA was 1.2, implying that OA in solution mainly existed in deprotonation form with negative charge at pH range from 2.9 to 8.9. As pH increased, the surface possessed more negative charges. As shown in Figure S8d, the OA adsorption decreased from 17% to 7% when pH increase from 2.9 to 8.9. The inhibition of catalytic activity might be due to the electrostatic repulsion between catalyst and OA.

Moreover, Co_{SAC}-N-C showed much higher O₃ decomposition rate compared to O₃ and N-C/O₃ system (Figure S9a), suggesting that more O₃ was activated and decomposed on Co_{SAC}-N-C. The electrochemical linear-sweep voltammetry (LSV) behavior of Co_{SAC}-N-C and N-C were investigated comparatively in the presence of O₃. As presented in Figure S9b, compared with NC, a higher reduction current density was observed in Co_{SAC}-N-C/O₃ system, implying the improvement of electron transfer on Co_{SAC}-N-C with O₃ decomposition [30]. Besides, for ozonation alone, the solution pH remains around 2.9–3.0 during degradation process because OA, an acid molecule, was not removed effectively (Figure S9c). When Co_{SAC}-N-C catalyst was added, the solution pH increased obviously from 2.9 to 4.7 because the acid molecule of

OA was mineralized effectively, suggesting its excellent mineralization activity. Furthermore, the Co_{SAC}-N-C/O₃ achieved more than 90% TOC removal within 60 min in the presence of environmental-relevant compound such as common anions (e.g., Cl⁻, SO₄²⁻ and NO₃⁻) and the natural organic matter (e.g., humic acid, HA) in Fig. 3f, indicating that Co_{SAC}-N-C/O₃ system exhibited efficient mineralization with coexisting environmental substance in wastewater. To verify the effective removal for general pollutants in Co_{SAC}-N-C/O₃ system, the degradation performance was further examined for the removal of other refractory pollutants with different molecular structures, including levofloxacin (LVFX), carbamazepine (CBZ), 4-nitrophenol (4-NP) and acetaminophen (APAP). The Co_{SAC}-N-C HCO process achieved almost 100% degradation efficiency and 44–58% TOC removal (Figure S10) with limited adsorption contribution for those pollutants, which suggested that Co_{SAC}-N-C/O₃ system exhibited broad generality for organic pollutants removal.

The above results indicated that Co_{SAC}-N-C showed excellent activity in activating ozone to degrade pollutants. Furthermore, the reusability of Co_{SAC}-N-C was investigated by multiple runs of the catalytic ozonation process. After each cycle, the catalyst was recovered by rinsing with ultrapure water and ascorbic acid solution, and then reused after drying. The next cycle started after recovered process. As presented in Figure S11a, OA mineralization efficiency in Co_{SAC}-N-C/O₃ system still remained above 86% after five consecutive cycles, implying the excellent stability and reusability of the Co_{SAC}-N-C catalyst. Moreover, the metal leaching of Co ion was lower than 0.010 mg/L (0.02 wt% of fresh Co_{SAC}-N-C catalyst). No obvious change in crystalline structure and morphology was observed after repeated reaction, suggesting the structural stability of Co_{SAC}-N-C (Figure S12).

3.3. Identification of reactive species and catalytic sites

The in-situ Raman was carried out to clarify the reactive species

adsorbed on catalysts surface. As shown in Fig. 4a, a characteristic peak appeared at 936 cm^{-1} upon ozone addition on $\text{Co}_{\text{SAC}}\text{-N-C}$, which was assigned to surface atomic oxygen species $^*\text{O}$ with the redox potential of 2.43 V [4,9,31–33]. On the contrary, the peak was not detected on N-C with or without ozone. These results suggested that O_3 can be decomposed into nonradical $^*\text{O}$ by single atom Co sites of $\text{Co}_{\text{SAC}}\text{-N-C}$. Furthermore, the EPR measurement was conducted to detect the reactive oxidant species (ROS) in HCO process. The DMPO reagent served as spin-trapping agent for radicals ($\cdot\text{OH}$ and $\cdot\text{O}_2$) [34,35]. As exhibited in Fig. 4b, a typical four-fold peaks of DMPO- $\cdot\text{OH}$ appeared in $\text{Co}_{\text{SAC}}\text{-N-C}/\text{O}_3$ and N-C system, indicating that both catalysts were able to produce $\cdot\text{OH}$. The characteristic signals of DMPO- $\cdot\text{O}_2$ adducts were not discovered in pure ozonation and HCO process (Figure S13a), excluding the generation of $\cdot\text{O}_2$. Besides, the TEMP was employed as spin-trapping agent to capture $^1\text{O}_2$ [36,37]. No obvious triplet signals were detected in $\text{Co}_{\text{SAC}}\text{-N-C}/\text{O}_3$ system (Figure S13b), suggesting that $^1\text{O}_2$ may not be involved in HCO system. The results indicated that $\text{Co}_{\text{SAC}}\text{-N-C}/\text{O}_3$ system involved both $^*\text{O}$ nonradical and $\cdot\text{OH}$ radical oxidation pathways. To determine the contribution of nonradical and radical species for OA degradation, chemical quenching experiments

were conducted with different scavengers. *Tert*-Butanol (TBA) was chosen as the scavenger of $\cdot\text{OH}$ and dimethyl sulfoxide (DMSO) was used to scavenge both $\cdot\text{OH}$ and $^*\text{O}$ [7,38]. The quenchers of TBA ($k_{\text{TBA}/\text{O}_3}=3\times 10^{-3}\text{ M}^{-1}\text{s}^{-1}$) and DMSO ($k_{\text{DMSO}/\text{O}_3}=0.42\text{ M}^{-1}\text{s}^{-1}$) showed slow reaction with ozone [7]. The addition of TBA (2 mM) was enough to quench the generated $\cdot\text{OH}$ because $\cdot\text{OH}$ probe of *para*-chlorobenzoic acid (*p*-CBA) consumption was completely inhibited with the addition of TBA in $\text{Co}_{\text{SAC}}\text{-N-C}$ HCO system (Figure S13c). As presented in Fig. 4c-d, the OA degradation rate was decreased by 58% after adding TBA, while the presence of DMSO caused significant suppression with degradation rate declining by 82%. This phenomenon confirmed that both $\cdot\text{OH}$ and $^*\text{O}$ simultaneously contributed to OA degradation in $\text{Co}_{\text{SAC}}\text{-N-C}/\text{O}_3$ system.

Moreover, *p*-CBA was selected as $\cdot\text{OH}$ probe because it showed rapid reaction with $\cdot\text{OH}$ ($k_{\text{p-CBA}/\cdot\text{OH}}=5\times 10^9\text{ M}^{-1}\text{s}^{-1}$) but was inert to ozone ($k_{\text{p-CBA}/\text{O}_3}\leq 0.15\text{ M}^{-1}\text{s}^{-1}$) [39,40]. As shown in Figure S13d, $\text{Co}_{\text{SAC}}\text{-N-C}$ and N-C HCO systems showed higher reaction rate with *p*-CBA than that of sole ozone, implying that both $\text{Co}_{\text{SAC}}\text{-N-C}$ and N-C can catalyze ozone to generate $\cdot\text{OH}$. The consumption rate of *p*-CBA in $\text{Co}_{\text{SAC}}\text{-N-C}$ system was similar with that in NC system, which was attributed to the close

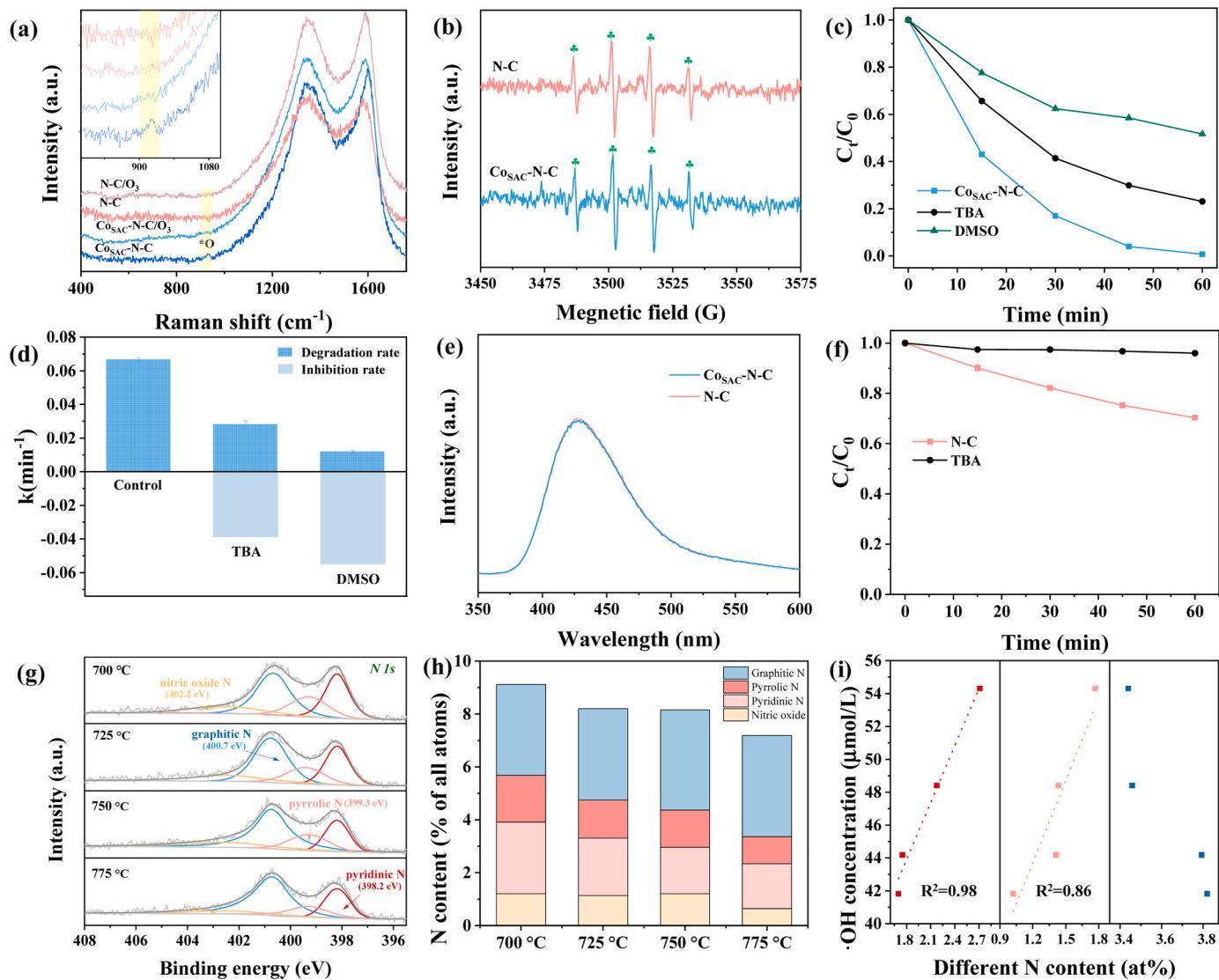


Fig. 4. (a) In-situ Raman spectra of $\text{Co}_{\text{SAC}}\text{-N-C}$ and N-C. (b) EPR spectra of DMPO- $\cdot\text{OH}$. (c) Quenching tests of reactive species during the OA removal in $\text{Co}_{\text{SAC}}\text{-N-C}/\text{O}_3$ system. (d) and their kinetic rate constants. (e) Fluorescence spectroscopy in catalytic ozonation at 10 min. (f) OA degradation by N-C with or without addition of TBA. (g) High-resolution XPS N 1 s spectra of $\text{Co}_{\text{SAC}}\text{-N-C}$. (h) Contents of compositional N species. (i) Relationships between $\cdot\text{OH}$ yields and the contents of different N species of $\text{Co}_{\text{SAC}}\text{-N-C}$. (Condition: $[\text{Co}_{\text{SAC}}\text{-N-C}]=50\text{ mg/L}$, $[\text{O}_3]=20\text{ mg/L}$, $[\text{OA}]=200\text{ mg/L}$, initial $\text{pH}=2.9$, $[\text{TBA}]=2\text{ mM}$, $[\text{DMSO}]=20\text{ mM}$).

$\cdot\text{OH}$ generation rate. Furthermore, the $\cdot\text{OH}$ can be determined by fluorescence spectroscopy with adding probe of terephthalic acid (TA), which can trap $\cdot\text{OH}$ to produce 2-hydroxyterephthalic acid (2-HTA) with strong fluorescence characteristics [41,42]. As presented in Fig. 4e, CoSAC-N-C showed similar signal intensity with N-C , indicating that introduction of Co single atom in N-C could not catalyze O_3 to generate $\cdot\text{OH}$. In $\text{N-C}/\text{O}_3$ system, $\cdot\text{OH}$ was the main species because the OA degradation was completely inhibited by TBA (Fig. 4f), in which N sites with free electrons was reported to be ascribed to $\cdot\text{OH}$ generation [20, 43]. The $\cdot\text{OH}$ production might be driven from N sites on carbon in HCO process. To further reveal the role of different N species in CoSAC-N-C for $\cdot\text{OH}$ production in catalytic ozonation, the correlation between N content and $\cdot\text{OH}$ yield was evaluated. As presented in Fig. 4g, the N1s spectrum of catalyst can be deconvoluted into four peaks at 398.2, 399.3, 400.7 and 402.2 eV, which were assigned to pyridinic-N, pyrrolic-N, graphitic-N and nitric oxide, respectively [43]. The content of N species in carbon catalyst could be changed with different pyrolysis temperatures. With increasing pyrolysis temperatures of CoSAC-N-C , total N contents decreased slightly, of which the pyridinic-N and pyrrolic-N gradually decreased while graphitic-N slightly increased (Fig. 4h and Table S5). The yield of $\cdot\text{OH}$ was measured by oxidizing salicylic acid (details in Text S4) [8]. As shown in Fig. 4i, the contents of pyridinic/pyrrolic-N were positively correlated to the $\cdot\text{OH}$ yield, revealing the pyridinic-N and pyrrolic-N were responsible for $\cdot\text{OH}$ generation rather than the graphitic-N. Besides, other possible sites, such as the O content and defect sites (represented by I_D/I_G), were not responsible for $\cdot\text{OH}$ generation because O content and I_D/I_G variation showed no obvious correlations with $\cdot\text{OH}$ yields as shown in Figure S14. Therefore, it is reasonably concluded that pyridinic and pyrrolic N served as active sites for $\cdot\text{OH}$ generation.

Based on above results, we found that the dual active sites of N sites and atomically dispersed Co sites were the origin of the high activity of

CoSAC-N-C : (1) The pyridinic and pyrrolic N functioned as radical-production sites to decompose O_3 into $\cdot\text{OH}$, which can degrade organic pollutants via radical oxidation pathway, and (2) the atomically dispersed Co sites promoted O_3 decomposition to produce $^*\text{O}$, which could remove pollutants by nonradical oxidation process. The synergistic function of N sites and single atom Co sites for concerted radical-nonradical oxidation pathways enabled efficient mineralization of pollutants in CoSAC-N-C HCO process. During the radical-nonradical oxidations, the pollutants could be firstly destructed by $\cdot\text{OH}$ into small organic acids, such as oxalic acid commonly produced as main degradation intermediates in HCO process, and then it was further mineralized by $^*\text{O}$. To confirm this supposition, we investigated the mineralization of aromatic pollutants (such as phenol) during $\cdot\text{OH}$ -dependent $\text{N-C}/\text{O}_3$ system, CoSAC-N-C with concerted radical-nonradical pathways showed higher mineralization performance towards phenol as well as the generated OA. Therefore, the synergistic oxidation of $\cdot\text{OH}$ and $^*\text{O}$ endowed CoSAC-N-C catalyst with efficient mineralization of organic pollutants.

3.4. Insight into radical and nonradical generation mechanism

To further elucidate the roles of N sites and atomically dispersed Co sites, density functional theory (DFT) calculations were performed to gain insight into O_3 activation over CoSAC-N-C catalyst. Based on charge difference, the binding sites of active center with ozone molecules were predicted by electrostatic effects, which was analyzed by using electrostatic potential (ESP) [6,17]. Fig. 5a showed ESP maps of ozone molecule and CoSAC-N-C catalyst. Accordingly, the ESP of mediate O (type I, O_1) in O_3 was positive, while the terminal O (type II, O_{II}) was negative. As for CoSAC-N-C , the central cobalt atom in the Co-N_4 moiety had the highest positive potential, which could serve as active sites to

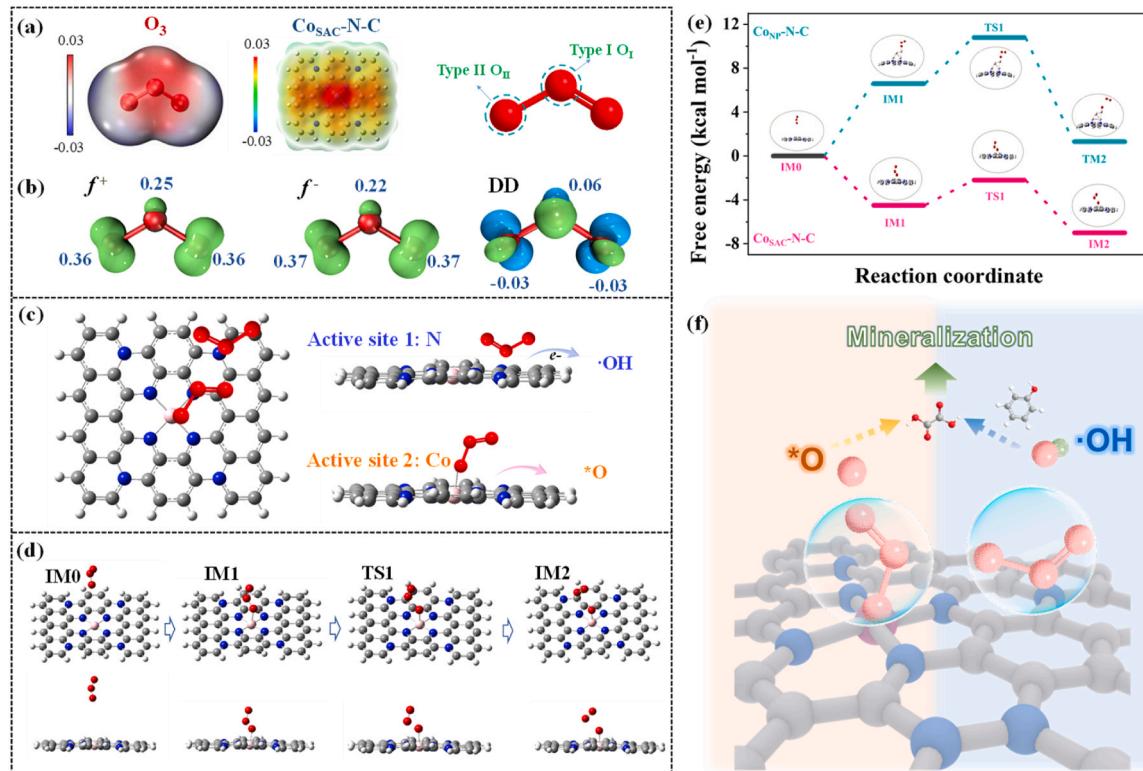
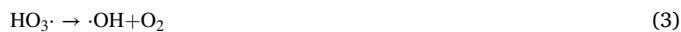


Fig. 5. (a) ESP maps of O_3 and CoSAC-N-C structure. (b) Fukui function and DD of O_3 . (c) Generation of reactive species on different sites. (d) Reaction process of O_3 decomposition on CoSAC-N-C for $^*\text{O}$ generation and optimized configurations of proposed intermediates. (e) Potential energy profile of the reaction pathway for $^*\text{O}$ generation on CoSAC-N-C and CoNP-N-C . (f) Proposed mechanism for radical-nonradical oxidation in CoSAC-N-C HCO process (gray for C, blue for N, red for O and green for H).

attract the terminal O_{II} atoms of O_3 . The N sites had negative ESP, which could be attractive to mediate O_I in O_3 . Moreover, the electronegativity values of N (3.04) was much higher than that of Co (1.88), in which N sites with higher electronegativity were more likely to attract and seize electrons in Co center forming dual-sites of electron-rich N (Mulliken charges -0.18) and electron-deficient Co (Mulliken charges $+1.23$) [17, 20]. For electron-rich N sites, the Mulliken charges increased from -0.18 to -0.14 after contacted with ozone, suggesting that N sites supplied electrons to ozone molecule for $\cdot OH$ production.

The local electrophilicity and nucleophilicity of sites can be described by dual descriptor (DD) and Fukui functions (f_+ and f_-). The active sites with positive value of DD showed more electrophilicity, while the sites with negative value were more nucleophilic [17, 44]. As shown in Fig. 5b, the Fukui functions f_+ and f_- of O atoms in O_3 molecule were positive, demonstrating that all the O atoms were both electrophilic and nucleophilic [17]. The DD of O_I in O_3 was positive, indicating mediate O_I atom was more electrophilic than nucleophilic and can be attracted to electron-rich N sites for $\cdot OH$ generation. By contrast, the DD of O_{II} in O_3 was negative, demonstrating that terminal O_{II} atoms had more nucleophilicity and were preferentially adsorbed on the positively charged Co sites of $Co_{SAC}-N-C$ with cleavage of O-O in O_3 for *O production. The O_3 was adsorbed on dual sites with different bonding configurations for radical and nonradical species generation, of which the mediate O_I in O_3 tended to be bonded on electron-rich N (active site 1) inducing $\cdot OH$ formation, while terminal O_{II} in O_3 was attracted on electron-deficient Co (active site 2) triggering *O generation (Fig. 5c).

To further investigate the interaction between O_3 and active sites, we calculated the Gibbs free energy for elementary step in O_3 decomposition on N and Co sites. The free energy diagrams were shown in Figure S16 and Fig. 5d. The electron-rich N sites can provide electrons to O_3 for $\cdot OH$ generation through radical chain reaction, which was favorable in thermodynamics [45]. After obtaining electrons from N sites, O_3 was transformed to $\cdot O_3$. Then $\cdot O_3$ can react with H_2O to generate $HO_3\cdot$, which can be dissociated to $\cdot OH$ and oxygen (Eqs. (1)–(3)). The O_3 was firstly adsorbed on Co sites with attachment of terminal O_{II} atom. Next, the O-O in O_3 was stretched and dissociated on Co sites, generating *O and a dioxygen molecule (Eq. (4)) [19]. As illustrated by the energy change plot for different steps, the Gibbs free energies for formation of *O on Co sites during O_3 activation by $Co_{SAC}-N-C$ were much lower than the initial form (Fig. 5e), demonstrating that the reaction was favorable in thermodynamics. Contrarily, the generation of *O on $Co_{NP}-N-C$ was an endothermic process and cannot occur automatically. It could be concluded that single atom Co sites induced *O formation rather than Co nanoparticle, which might result from the unique electronic structure of single Co atoms in $Co_{SAC}-N-C$ catalyst.



The calculation results were basically consistent with the experiment results of in-situ Raman, EPR and scavenging experiments. Based on the results, we proposed a synergistic radical-nonradical catalysis mechanism on $Co_{SAC}-N-C$ with dual-active sites during catalytic ozonation process (Fig. 5f). The electron-rich N sites was attractive to the mediate O_I atom of O_3 molecule, supplying electrons to O_3 for $\cdot OH$ generation through radical chain reaction. Meanwhile, the terminal O_{II} of O_3 preferred bonding with electron-deficient Co sites triggering nonradical *O generation by O-O cleavage. Such different O_3 adsorption configuration at dual active sites facilitated $\cdot OH$ and *O generation. The synergistic function of N sites and single atom Co sites for concerted radical-nonradical oxidation pathways endowed $Co_{SAC}-N-C$ catalyst with excellent performance for pollutants removal.

3.5. HCO performance in practical wastewater treatment

The treatment of coking plant secondary effluent was inspected to evaluate application potential of the dual-site catalyst for practical wastewater treatment. The experiment was conducted in a continuous-flow reactor (Fig. 6a-b) filled with $Co_{SAC}-N-C$ -loaded alumina spherules (detailed information was shown in Text S1 and Figure S17). And the secondary effluent wastewater was obtained from a coking plant in southern China. The details of physicochemical properties in the wastewater were given in Table S6. The removal efficiency of chemical oxygen demand (COD) and UV_{254} were used to evaluate the water purification capacity. The initial COD value of the real wastewater was around 86 mg/L. The effluent COD was lower than 50 mg/L persistently with the removal efficiency of 42–51% after 40 min treatment (Fig. 6c), which stably met level A of first Class given in the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant in China (GB 18918–2002, COD < 50 mg/L), indicating the promising application potential for practical wastewater treatment. In addition, the result also revealed a high level of UV_{254} substance removal (~94%) (Fig. 6d), suggesting massive destruction or elimination of aromatic pollutants in this HCO process [5]. In the same experiment condition, the COD and UV_{254} removal by commercial activated carbon was lower than that by $Co_{SAC}-N-C$ -loaded alumina (Figure S18). Based on GC-MS analysis, the organic pollutants in the coking wastewater mainly consisted of decane, lactone, phenols and docosenoamide components. Detailed information of major organics was listed in Table S7. The GC-MS results of the coking wastewater before and after catalytic ozonation treatment were shown in Fig. 6e and the major components removal was shown in Fig. 6f. It can be clearly observed that most components in effluent were effectively eliminated after treatment. Furthermore, 3D-EEM fluorescence spectroscopy was performed to analyze the changes of dissolved organic matter (DOM) in wastewater. As shown in Fig. 6g, the DOM in coking wastewater was mainly distributed in region II (Ex < 250 nm, Em < 380 nm), region III (Ex < 250 nm, Em > 380 nm) and region V (Ex > 250 nm, Em > 380 nm), corresponding to aromatic proteins, fulvic-like substance and humic-like substance with poor biodegradability, respectively [6]. As shown in Fig. 6h, all the 3D-EEM peaks for effluent of treated wastewater by $Co_{SAC}-N-C$ HCO system almost disappeared, indicating that the catalytic ozonation with $Co_{SAC}-N-C$ could effectively remove refractory organic pollutants in coking wastewater. In conclusion, the above results revealed the efficient $Co_{SAC}-N-C$ catalysts had an application potential applicability for practical wastewater treatment.

4. Conclusion

This study developed a catalyst of N-coordinated single cobalt atoms with dual active sites for efficiently catalytic ozonation process in a concerted radical-nonradical oxidation pathway. Specifically, the electric-rich N sites was attractive to the mediate O_I atom of O_3 molecule with supplying electrons to O_3 for radical $\cdot OH$ generation. Meanwhile, the terminal O_{II} of O_3 preferred bonding with electron-deficient Co sites, thus triggering nonradical *O generation by O-O cleavage. The synergistic oxidation of $\cdot OH$ and *O in the $Co_{SAC}-N-C$ HCO process enabled effective organic pollutants mineralization, surpassing most of conventional HCO catalysts. The experiments indicated that the organic pollutants could be firstly destructed by $\cdot OH$ into small-molecule intermediates and then were further mineralized by *O . Moreover, the concerted radical-nonradical process showed strong environmental tolerance to common anions (Cl^- , SO_4^{2-} and NO_3^-) and human acid in wastewater. For practical wastewater, $Co_{SAC}-N-C$ exhibited efficient decontamination of coking secondary effluent with COD reducing from 86 mg/L to less than 50 mg/L in the fixed-bed reactor. This work provided a viable strategy of developing highly efficient HCO catalysts with electron-rich sites and electron-deficient sites to promote synergistic radical-nonradical oxidations for advanced wastewater treatment.

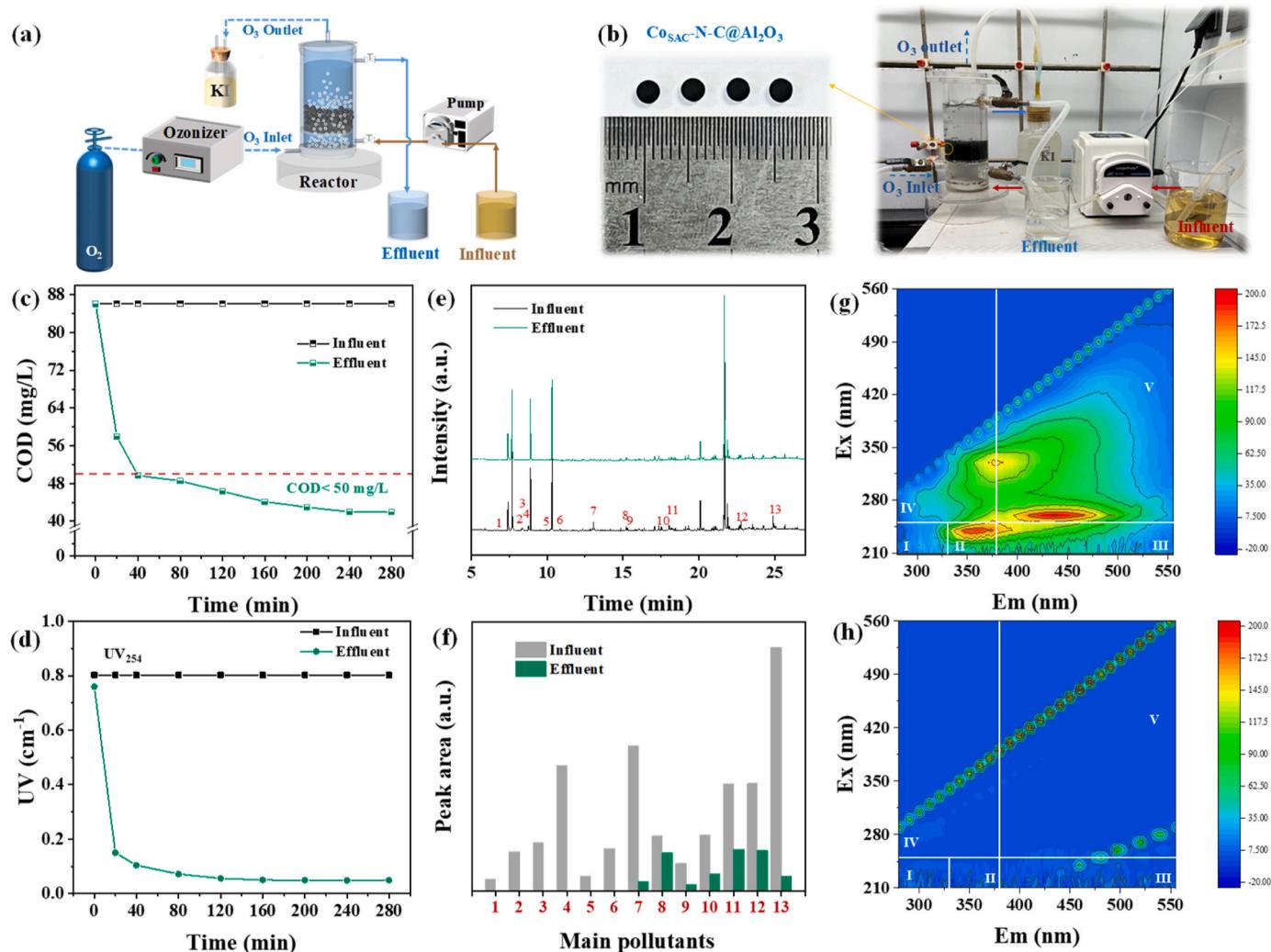


Fig. 6. (a) Schematic diagram of the continuous flow reactor. (b) Optical image for continuous flow reactor during treatment of coking wastewater. (c) COD values (d) and UV₂₅₄ during coking wastewater treatment in the continuous-flow reactor. (e) GC-MS analysis and (f) main pollutants removal during treatment of coking wastewater. (g) 3D-EEM results of influent and (h) effluent coking wastewater. (Coking wastewater treatment conditions: 200 g catalyst, [O₃]=10 mg/L, V=0.5 L, HRT=40 min).

CRediT authorship contribution statement

Hongtao Yu: Supervision, Resources. **Xie Quan:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Shuo Chen:** Resources, Project administration, Investigation. **Yanming Liu:** Validation, Supervision, Resources. **Lanlan Liang:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Peike Cao:** Writing – review & editing, Methodology, Conceptualization. **Haokun Bai:** Supervision, Investigation, Formal analysis. **Xin Qin:** Supervision, Methodology, Data curation. **Zijie Lu:** Visualization, Supervision, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.124149.

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